

# The influences of gypsum water-proofing additive on gypsum crystal growth

Jianquan Li, Guozhong Li<sup>\*</sup>, Yanzhen Yu

*College of Material Science and Engineering, Jinan University, 250022 Jinan, Shandong, China*

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## Abstract

The gypsum water-proofing additives were composed of organic emulsion that were emulsified by polyvinyl alcohol and stearic acid and saline water-proofing additive made of alunite, carboxylic acid sodium, aluminium sulfate, etc. Using modern testing instrument, such as SEM, EPS, the influences of gypsum water-proofing additives on the crystal growth of gypsum products and its water-proof mechanism were analyzed from the perspective of the crystal changing of gypsum after adding gypsum water-proofing additive. Such results show that organic emulsion can be adsorbed selectively on the gypsum crystal surface, inhibiting the crystal growth along axis *c*. Besides, anion  $\text{RCOO}^-$ , cations  $\text{Na}^+$  and  $\text{Al}^{3+}$  in saline water-proofing additive can be adsorbed selectively to crystal section (111) to coordinate, slowing down the growth speed along axis *c*, which could balance the speed in all directions and turn the crystal into a short hexahedron pole.

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## 1. Introduction

At present, all kinds of gypsum products are widely used in the building trade because of their various fine performances. However, their low strength and weak performances in both water-proof and damp proof are clearly found [1]. The water-absorbing rate of the ordinary gypsum products is generally about 50%, and the intenerate coefficient is only about 0.2–0.3, so the products are easily deformed after being dampened; besides, it causes building walls to soften and rot. Those shortcomings have been greatly hampering the development of the gypsum products.

For this reason, a large amount of research [1–7] on the water-proof performance of gypsum products has been carried out at home and abroad, and a great deal of achievements have been made. One method was to mix organic water-proofing additive agent (such as silica gel) into gypsum materials in order to reduce the water-absorbing rate of the gypsum material; another was to add cement directly into the building gypsum so that the gypsum could be transformed into a water rigid material. Unfortunately, the results of those methods were unsatisfactory. Later new methods were tried, such as painting an organic water-proofing

additive on the gypsum board or choosing a water-proof layer, but they just had a temporary effect, and failed to solve the fundamental water-proof problem of the gypsum products.

Here, a new type of gypsum water-proofing additive was created by emulsifying polyvinyl alcohol and stearic acid together, and mixing with alunite, carboxylic acid sodium, aluminium sulfate, etc. as the saline water-proofing additive. This new water-proofing additive turned out to be quite satisfactory. It can be mixed with gypsum and water directly and causes the crystallization of the gypsum. Recently, too much attention was paid only to the water-proofing additive and the effects; researches only analyzed the reason, theory and the mechanism, ignoring the crystallization process. They omitted the influences of the gypsum water-proofing

Table 1  
Composition of the raw material

Sample number	Gypsum (g)	Organic emulsion (ml)	Saline water-proofing additive (g)	Water (ml)
1	1200	0	0	750
2	1200	0	12	750
3	1200	60	0	690
4	1200	60	12	690

<sup>\*</sup> Corresponding author. Tel.: +86 531 8276 5974.

E-mail address: [ligz5974@163.com](mailto:ligz5974@163.com) (G. Li).

Table 2  
Performances of the samples

Sample number	Water-absorbing ratio	Crystal appearances	2 h strength/MPa		24 h strength/MPa	
			Bend strength	Compressive strength	Bend strength	Compressive strength
1	41.30%	Long club shape	3.17	6.92	3.78	8.75
2	15.96%	Short pole shape	4.05	8.05	4.42	9.21
3	6.08%	Short club shape	2.67	5.65	3.20	7.35
4	3.57%	Short pole shape	3.25	6.49	3.61	8.31

additive on the crystallization and the water-proof effect, etc. As regards to this purpose, we carried out the following research.

## 2. Raw materials and experiment method

### 2.1. Raw materials

The building gypsum produced in Shandong Pingyi Jinxin Gypsum Company of China was chosen.  $\text{SO}_3$  holds 41.9% and the crystal water 16.5%, the mass ratio of water and gypsum of standard denseness is 0.65, and the ratio surface area stands  $4122 \text{ cm}^2/\text{g}$ .

The compound gypsum water-proofing additive was produced by adding saline water-proofing additive into the organic emulsion of polyvinyl alcohol, stearic acid and wax. The saline water-proofing additive was composed of alunite, carboxylic acid sodium, aluminium sulfate with the percentage of weight of 1:0.8:0.5.

### 2.2. Experimental techniques

Contradistinctive methods were employed to analyze the influences of the gypsum water-proofing additive on gypsum

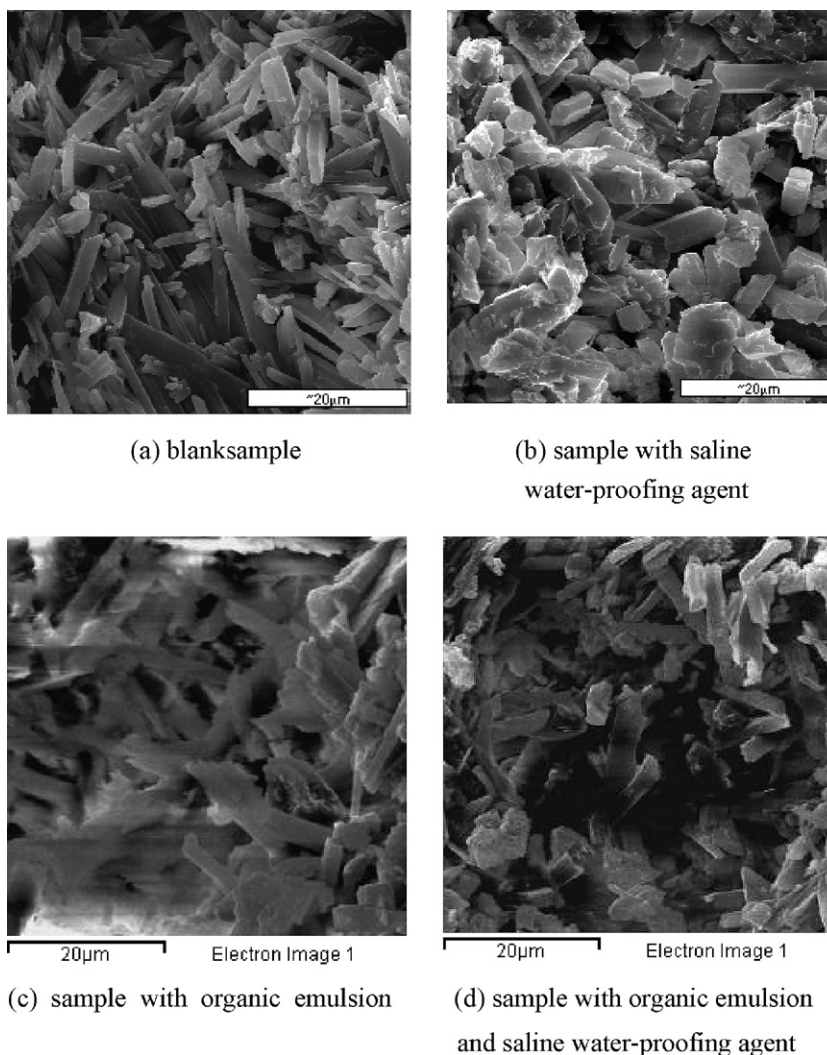


Fig. 1. Influences of gypsum water-proofing additive on dihydrate gypsum crystal appearances.

crystal formation. The composition of the raw materials are shown in Table 1.

### 2.3. Samples shaping

First, weigh the raw materials according to Table 1; next, add the gypsum water-proofing additive into JSA-195 stirrer with water, and stir evenly; then pour the gypsum powder quickly and stir for 2 min; finally pour the plaster into a triplicate model to shape by vibration. After 1 h, unmold the samples and cure in a standard conservatory.

### 2.4. Experimental methods

#### 2.4.1. Building gypsum performance testing

Test the performances of building gypsum according to GB9776-88 in China.

#### 2.4.2. Observation of gypsum crystal shape appearance

Use the S-2500 scanning electron microscope (SEM) to observe the crystal shape appearance of the original sections of the gypsum-hardened body.

#### 2.4.3. Electronic energy spectrums testing

The multi-functional EPS energy spectrum instrument was adopted to measure the energy and intensity of the characteristic elements on the gypsum surface before and after adsorbing the gypsum water-proofing additive, and then the features of the gypsum water-proofing additive on the gypsum surface were analyzed.

## 3. Experimental results and discussions

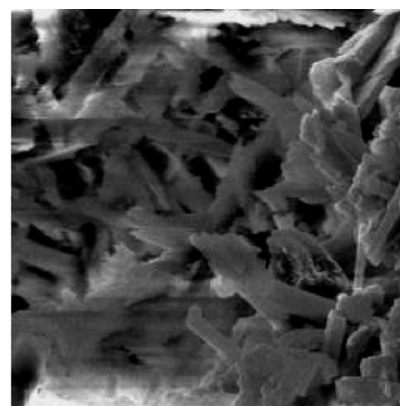
### 3.1. Experimental results

Table 2 shows the results of the samples made according to Table 1. The crystal of the blank sample appears as a long club shape with a water-absorbing ratio of 41.3%. After the addition of a certain amount of saline water-proofing agent and organic emulsion respectively, the crystals turn out to be short pole shape and short club shape respectively, and the water-absorbing ratio reduced to 15.26% and 5.27%. Besides, the strength of the sample with saline water-proofing agent was increased. When those two materials were added simultaneously, the crystal became short pole shape with the water-absorbing ratio reducing to 3.28%, and the strength reduced slightly, comparing to that of the blank sample.

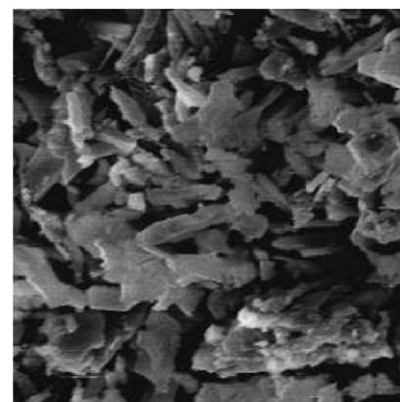
### 3.2. Influence of gypsum water-proofing additive on dihydrate gypsum crystal appearances

Fig. 1 clearly shows the changes of the appearance of dihydrate gypsum crystals. Fig. 1(a) provides a typical kind of gypsum crystal appearance, whose needle crystal of big length–radius ratio interweaves together vertically and horizontally. After a saline water-proofing additive was added, see Fig. 1(b), all gypsum crystals turned out to be a sort of short pole shape, and needle crystals can hardly be found. At that time, the crystals were thick, the structure was closely knitted, and the ratio surface area was much smaller. As a result, the improvement of gypsum-hardened body strength became possible. After organic

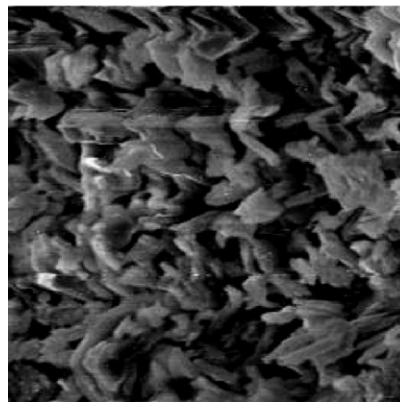
emulsion was added, see Fig. 1(c), the surface of the crystal became rough and turned out to be a strip crystal of much smaller length–radius ratio instead of regular crystal shape. The structure between the crystals was closely knitted, and the organic emulsion spread evenly on the surface of the crystal. Fig. 1(d) provided a picture of the samples with organic emulsion and saline water-proofing additive. Due to the influences of the organic emulsion and saline water-proofing additive on the growth of the crystal, the surface of the crystal became slightly coarse, and the shape turned out to be between needle and short pole.



Electron Image 1  
(a) 5% organic emulsion



Electron Image 1  
(b) 10% organic emulsion



Electron Image 1  
(c) 15% organic emulsion

Fig. 2. Influences of organic emulsion in different percentages on gypsum crystal appearances.

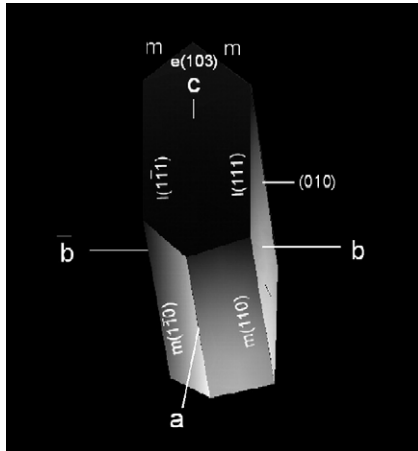


Fig. 3. Appearance of monocline dihydrate gypsum crystal.

### 3.3. Influences of organic emulsion in different percentage on gypsum crystal appearances

Three different mixings of organic emulsion of 5%, 10% and 15% were respectively chosen. The changes of the gypsum crystal shape appearance as the amount of organic emulsion became different were observed. Fig. 2 shows the results.

In Fig. 2, it was clearly seen that the shape appearances of dihydrate gypsum crystal changed with the amount of the organic emulsion changing. As the amount increased, the crystal shape gradually changed from slender needle to short pole, and the transverse size of the crystal presented the increasing trend constantly. This proved that organic emulsion inconsistently inhibited the growth of the gypsum crystal at each axis. Obviously, when the long axial growth was strongly inhibited, the relative growth rate of the short axis and the long one was gradually getting closer, and at the same time the crystal gradually turned out to be a kind of pole shape. When a large amount was mixed, the crystal nearly turned into angular cubes.

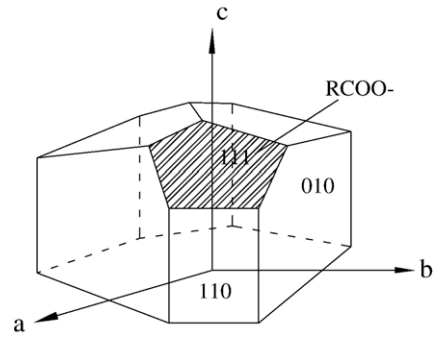


Fig. 5. Adsorption of  $\text{RCOO}^-$  base group.

### 3.4. Function mechanism of gypsum water-proofing additive

#### 3.4.1. Crystal structure of dihydrate gypsum

Dihydrate gypsum belongs to the monocline crystal series [1–4,9]. A double-layer structure with  $\text{H}_2\text{O}$  molecule distributing between them is formed through the connection of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  tetrahedron. Consequently, the layer structure forms alternatively with ion combining layers of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  and that of  $\text{H}_2\text{O}$  molecules.

In different crystal axial directions, the bonding form and ability of  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  are consistently different. The growth rate differs greatly and different crystal sections form. In the axis  $c$  direction,  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  respectively have two complete bonds, which make the bonding even more stable. In addition, two free ends can form bonds, which improves the rapid growth of this crystal section. Due to the little surface area of (111), it frequently disappears. A typical double symmetrical monocline dihydrate gypsum crystal is shown in Fig. 3 [9]. The growth rate of those three crystal sections is compared: section (111) > section (110) > section (010). Additionally, elements in different sections are not the same. In (111),  $\text{Ca}^{2+}$  is found, while in (110),  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  are found.

#### 3.4.2. Function mechanism of organic emulsion

It is also clearly shown in Fig. 2 that the inhibiting effect of organic emulsion on the growth speed of the gypsum crystal in each growth

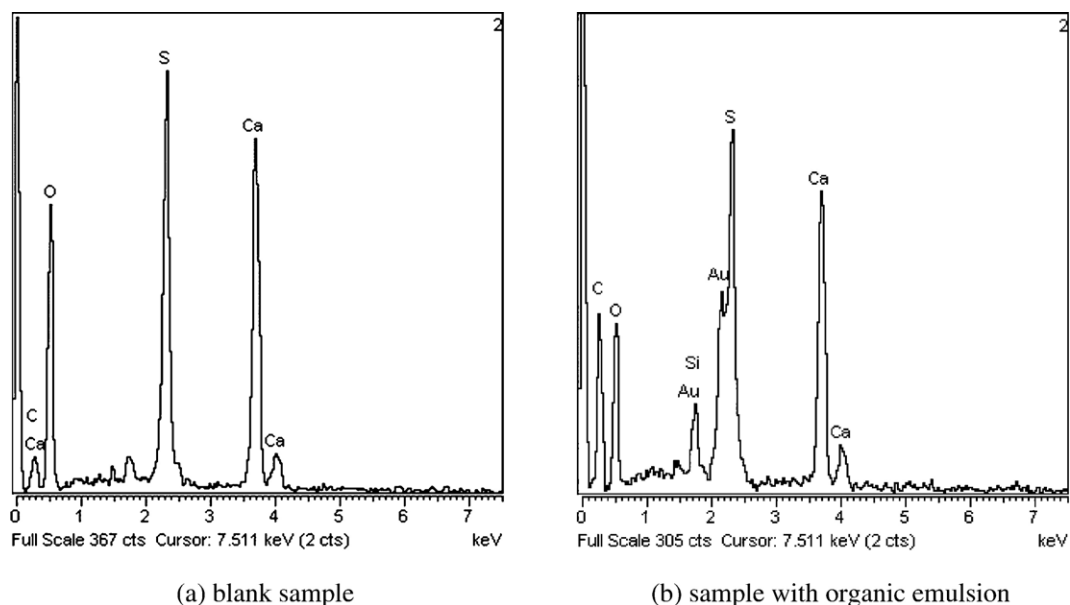


Fig. 4. Element distributing on gypsum crystal surface.



direction is different. The organic emulsion strongly inhibited the growth in long axis  $c$ , thus the relative growth speed in each crystal section turned out to be changed, and the crystal got short and thick. When organic emulsion was not added, dihydrate gypsum crystal in axis  $c$  grew the fastest, while that in axes  $a$  and  $b$  grew much slower. As a result, the crystal turned out to be needle shaped. Whereas, after mixing organic emulsion, the crystal in direction  $c$  got short and that in directions  $a$  and  $b$  much thicker. Furthermore, crystals became flatter and thicker as more and more organic emulsion was added. Therefore it could be inferred that it has much to do with the choice adsorption of organic emulsion. It was the choice adsorption that produced thick gypsum grain structures, which had strong hydrophobic ability. At that time, the organic emulsion arranged itself directionally on the gypsum grain surface, and the hydrophobic groups were unanimously outside toward. The water-proof goal could be achieved. To prove this further, energy spectrum EPS was adopted to analyze the changes of the elements on a gypsum surface before and after adsorption respectively. As Fig. 4 shows, quite few carbon elements (coming from organic emulsion) on the crystal surface could be found before adsorption, while after adsorption, carbon elements increased significantly. It was due to the increase of organism on gypsum crystal surface that the macro water-proof performance of gypsum could be improved.

#### 3.4.3. Function mechanism of saline water-proofing additive

The saline water-proofing additive used in this experiment was produced by compounding many types of organic and inorganic salt, such as  $\text{Na}^+$ ,  $\text{Al}^{3+}$ , carboxylic acid and anion. When those salts were added, both the functions of cation and anion groups, which had strong sorption, were taken into account. For example, Fig. 5 [7–9] shows the selective adsorption of the additive agent to section (111). This additive agent is compounded by plural carboxylic acid anion  $\text{RCOO}^-$  and its cations  $\text{Na}^+$ ,  $\text{Al}^{3+}$ . After the dissolution of an additive agent containing carboxylic acid salt, net structures formed in which one end of the  $\text{RCOO}^-$  base group is adsorbed and linked with  $\text{Ca}^{2+}$  of crystal (111) while the other end with  $\text{Al}^{3+}$ . In this way,  $\text{RCOO}^-$  of strong sorption ability could adsorb and coordinate with ions  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$  at the same time. As a result, nets “transitional membranes” of organic macromolecules adsorbing metal ions formed in section (111). According to the Periodic Bond Chain theory (PBC), it was very difficult for crystal growth base units to join crystal sections which own this kind of net membranes, because those units must destroy the existing sorption bonds of the membranes before joining with crystal sections. Thus the net membranes prevented crystal base units from joining the crystal section, which slowed down the growth rate of the gypsum crystal in direction  $c$ , but accelerated that in directions  $a$  and  $b$ . At that time, the growth rate in all directions became balanced, and the products turned out to be short hexahedron pole. It could be indicated that saline water-proofing additive agglutinating on the gypsum grains reduced the solubility of the gypsum and improved the water-proof performance. Meanwhile, the thicker crystal structure, the reduced porosity and the increased joining area between the gypsum crystals made a type of gypsum of sound strength possible, which was represented as water absorbing rate reducing and strength increasing from the macro view.

#### 3.4.4. Function mechanism of organic emulsion and saline water-proof acting together

During the reaction of the organic emulsion and saline water-proofing additive on the gypsum, one end of  $\text{RCOO}^-$  base groups of the latter adsorbed and linked with the  $\text{Ca}^{2+}$  of crystal section (111) while the other end reacted with  $\text{Al}^{3+}$  to form a network agglutinating

on section (111). In this way, a net “transitional membranes” layer of organic macromolecules adsorbing metal ions is formed, which inhibited the growth of the crystal in axis  $c$ , and the salt was adsorbed on the crystal surface which made the crystal structure more compact. Meanwhile, the organic emulsion was adsorbed on the gypsum crystal surface, which further inhibited the growth of the crystal in direction  $c$ . It also filled some non-closed gaps, making the gypsum's grain structure thicker. Consequently, the gypsum surface presented strong hydrophobic ability. Still, the organic emulsion arranges directionally on the gypsum's grain surface, and the hydrophobic groups were all unanimously outside toward. It could be said that the united action of organic emulsion and saline water-proofing additive can improve the water-proof performance of the gypsum and increase the strength.

## 4. Conclusions

- (1) The addition of a water-proofing additive changed the crystal shape appearance. In it the organic emulsion turned the crystal from needle shape into a short coarse stick and the saline water-proofing additive turned the crystal into a short pole.
- (2) Organic emulsion adsorbed selectively on the gypsum crystal surface, inhibiting the crystal growth along axis  $c$ ; it arranged directionally on the crystal surface, improving the water-proof performance of the gypsum.
- (3) Additive agent compounded by anion  $\text{RCOO}^-$  and cations  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$  in saline water-proofing additive can be adsorbed selectively to crystal section (111) to coordinate, slowing down the growth speed along axis  $c$ , which could balance the speed in all directions and turn the crystal into a short hexahedron pole. As a result, the water absorption rate declined and the strength increased.

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